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XXII. "On some new Ethyl-compounds containing the Alkali-metals." By J. A. WANKLYN, Esq. Communicated by EDWARD FRANKLAND, Ph.D. Received June 10, 1858.

(Abstract.)

The very remarkable composition and properties of that class of substances comprehending kakodyl and zinc-ethyl, have justly attached no ordinary degree of interest to the so-called organo-metallic compounds.

Influenced by that interest, I was led to inquire whether the series might not include members into whose composition the alkali-metals entered. It was a question whether combination between so powerfully electro-positive a body as potassium or sodium on the one hand, and a hydrocarbon radical on the other, did not involve impossible conditions. It seemed that the answer to this query would not be valueless as a contribution to the store of facts out of which we may hope some day to evoke the conditions of chemical combination.

My researches in this direction have already enabled me to produce combinations of ethyl with potassium and sodium; and I have little doubt that I shall be able to produce similar compounds containing lithium, barium, strontium, calcium, and magnesium. Combinations containing methyl in place of ethyl will also be sought. The present paper will be devoted chiefly to the ethyl-compound of sodium.

*Sodium-ethyl.*

Experiments made with a view to the formation of this body by reactions similar to that by which zinc-ethyl is produced, yielded negative results; but some months ago I made the observation that potassium and sodium decomposed zinc-ethyl, and I found the action to consist in the replacement of a portion of the zinc by the metal employed.

Sodium-ethyl was prepared as follows:—A tube of soft glass was closed at one end and filled with coal-gas. In it was then placed a single clean piece of sodium; its open extremity was then closed with the finger, and whilst still filled with coal-gas, the tube was contracted about the middle, drawn out and bent twice at right angles; pure zinc-ethyl, in quantity about ten times the weight

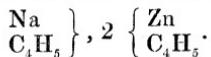
of the sodium, was next introduced, and the tube hermetically sealed. So prepared, the apparatus was afterwards placed in cold water, and left therein for several days, being cautiously shaken up at intervals.

During this time the following changes were noted in the contents of the tube. The sodium became coated with zinc, and gradually disappeared, whilst the total volume of the solid and liquid contents diminished considerably. The liquid became also viscid, and sometimes separated into two portions non-miscible with each other, becoming, however, homogeneous as the operation advanced. There was no evolution of gas.

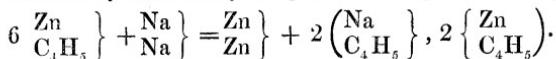
After the lapse of some days the apparatus was found to contain metallic zinc and a clear colourless liquid. The former was weighed and found to correspond to the sodium dissolved, one equivalent of zinc being precipitated for each equivalent of sodium dissolved.

The clear liquid was made the subject of special examination. It consisted of zinc-ethyl holding in solution a crystalline compound containing sodium, zinc, and ethyl. It was inflammable to the last degree, burning explosively, on exposure to the air, with a yellow flame, and leaving a very alkaline residue. Owing to its extreme tendency to become oxidized, its manipulation presented great difficulties. It was requisite to decant it into bulbs filled with dry hydrogen or coal-gas; and since heat produced partial decomposition, the bulbs had to be double, so that the heated bulb might not receive the liquid.

The clear liquid deposited large quantities of beautiful crystals when cooled to zero; and when gently warmed in a stream of dry hydrogen gas, so long as zinc-ethyl came off it yielded also a mass of crystals. Some crystals were prepared in the latter manner; they fused at about 27° C., but once fused they remained fluid at several degrees below that point. Numerous analytical determinations prove that these crystals contain two equivalents of zinc for every equivalent of sodium, and that their formula is



The reaction by which they are produced may be thus expressed :



For the body  $\text{NaC}_4\text{H}_5$  I propose the name *sodium-ethyl*, and for the crystals that of *double compound of sodium-ethyl with zinc-ethyl*.

Many attempts were made to obtain sodium-ethyl free from zinc-ethyl, but without success.

By distillation it was found to be equally impossible either to distil off  $\text{Na}_{\text{C}_4\text{H}_5}$  } from the crystals, or to distil off all  $\text{Zn}_{\text{C}_4\text{H}_5}$  } so as to leave pure  $\text{Na}_{\text{C}_4\text{H}_5}$  } behind. When the crystals are moderately heated in a bulb, a singular phenomenon occurs. Gas is evolved, and there remains behind metallic sodium, also metallic zinc, but no carbonaceous residue. This reduction of a sodium-compound by heat alone is an anomaly in chemistry.

When the crystals are heated in the water-bath with potassium, a sudden evolution of gas occurs, and there results metallic zinc, with a liquid alloy of potassium and sodium—a result likewise peculiar.

When the crystals are heated in the water-bath with excess of sodium, evolution of gas likewise takes place.

From these experiments it would seem that the conjoined zinc-ethyl is necessary to the existence of sodium-ethyl; or more precisely, that some adjunct of a less positive nature than sodium-ethyl is requisite to make the existence of the latter possible.

Passing on to the other reactions of the crystals  $2(\text{ZnC}_4\text{H}_5)$  } :—  
 $\text{NaC}_4\text{H}_5$

With water there is given pure hydride of ethyl, and hydrated oxides of zinc and sodium. The reaction takes place with great evolution of heat.

With carbonic acid there is given propionate of soda, which unites with zinc-ethyl forming a double compound, decomposed on the addition of water. To the account of this reaction, published elsewhere, I have to add that it takes place without evolution of ethyl or any other gas—a result which further confirms the formula of sodium-ethyl adopted in this paper.

With carbonic oxide there is also a reaction, which is in course of examination.

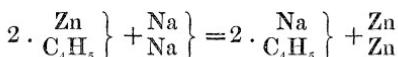
Cyanogen gas is instantly absorbed, with the formation of a brown solution.

With ether there seems to be no reaction. For the rest, with oxygen, iodine, &c., I should predict reactions quite analogous to those of zinc-ethyl, but have not specially examined the point.

*Potassium-ethyl.*

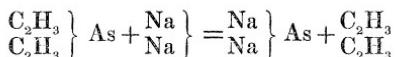
Zinc-ethyl and potassium react still more readily than the former body and sodium. So far as at present ascertained, the cases greatly resemble one another. Just as with sodium, I obtain crystals readily soluble in zinc-ethyl, which contain in this case abundance of potassium.

Seeing that the *kind* of reaction brought under notice in this paper is apparently unique, it is necessary to offer a few observations upon it.

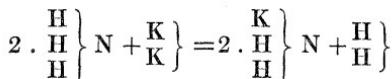


The reaction here formulated may be regarded as an electrolytic decomposition—as an ordinary case of precipitation of one metal by a more electro-positive metal. Here ethyl is the electro-negative, and zinc the electro-positive member: sodium is more electro-positive than zinc, and accordingly sodium displaces zinc.

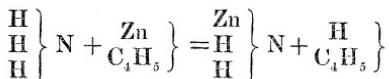
Following out the hypothesis—where the organo-metallic body contains a metal less electro-positive than the hydrocarbon radical, I should expect that the hydrocarbon radical would be eliminated by the action of sodium. Kakodyl, for instance, should give methyl and arsenide of sodium.



A case in point is afforded by the reaction of the alkali-metals with ammonia.



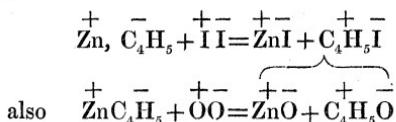
Of the same kind is the reaction of zinc-ethyl upon ammonia\*.



To develope the hypothesis still further: just as the positive side admits of displacement by a more electro-positive radical, so should the negative side admit of displacement by a more electro-negative body.

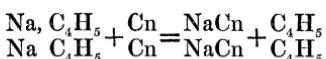
\* See Frankland's paper, Trans. Royal Soc. 1857.

The ordinary reactions of zinc-ethyl may be looked upon as illustrating this proposition, and can be written so as to exhibit a double displacement.



Inspection will show in all these cases, that an electro-positive radical displaces a less electro-positive radical; and an electro-negative radical displaces a less electro-negative one.

In accordance with the theory would be the displacement in sodium-ethyl of the ethyl by mercury, or by copper, &c., platinum, &c.



Also a like displacement by arsenic or by nitrogen would be according to theory.

Pushing the hypothesis to its furthest limits, I should say that sodium-ethyl is only in *equilibrium* with bodies whose respective electrical sides lie either both of them *within*, or both of them *without* the space lying between the electro-positive sodium and the electro-negative ethyl.

### XXIII. "Note on Sodium-ethyl and Potassium-ethyl." By EDWARD FRANKLAND, Ph.D., F.R.S. Received June 17, 1858.

The recent interesting discovery of sodium-ethyl and potassium-ethyl by Mr. Wanklyn, led me to investigate the cause of the non-formation of these bodies by reactions analogous to those successfully used for the production of zinc-ethyl and similar organo-metallic compounds. In my earlier experiments upon the isolation of the organic radicals, I studied the action of potassium and sodium upon iodide of ethyl, and found that the latter compound was readily decomposed by either of the metals at a temperature of from 100° to 130° C. The separated ethyl was, however, transformed almost completely into hydride of ethyl and olefiant gas, whilst not a trace of potassium-ethyl or sodium-ethyl was produced. Mr. Wanklyn has